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Research Article

Isolation and Characterisation of 2-Tert-butyl-8-hydroxyquinoline as a Crystalline Solid and Its Blue Fluorescent Li Complex

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2-Tert-butyl-8-hydroxyquinoline (2-TB-8-hq) has been isolated as a crystalline solid and its X-ray structure elucidated, resolving three decades of controversy, since it was previously wrongly reported as yellow oil by some other workers. An improved synthetic method has been developed which increases the yield from 20% to 60%. The lithium complex of 2-TB-8-hq is blue emitting and the HOMO and LUMO levels are lowered by 0.86 eV and 0.74 eV, respectively, compared with the parent lithium 8-hydroxyquinolinolate (Li 8-hq).

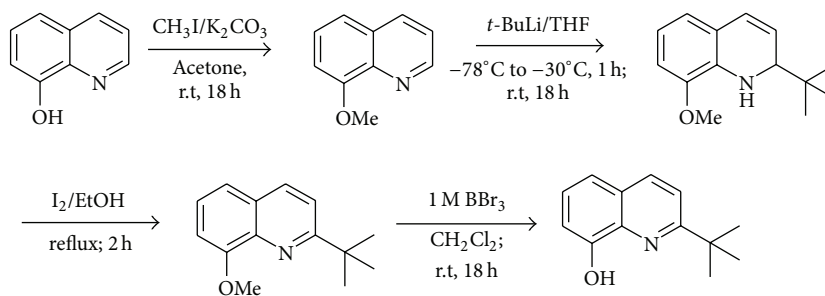
1. Introduction

8-Hydroxyquinoline (8-hq) and its derivatives have been the subject of intense study over the last thirty years because of their use in analytical chemistry, but more recently the focus of interest in this class of compounds has been expanded due to the use of metal complexes of 8-hq in high-efficiency multilayer organic light-emitting devices (OLEDs) [1].

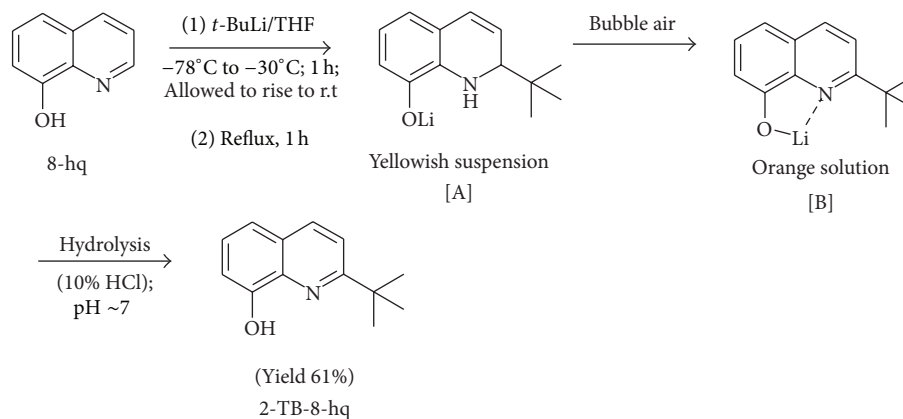
Metal complexes of 8-hq, aluminium quinolinolate (Alq_3), and zirconium quinolinolate (Zr_2q_4) have been extensively studied owing to their high stability and their application in commercial OLEDs [2–4]. Metal complexes of sterically hindered 2-substituted 8-hq have also attracted great interest [4–8] because of the possibility of colour tuning as well as ability to manipulate the HOMO-LUMO levels by forming mixed ligand complexes [7]. Aluminium does not form the usual tris complex with 2-substituted 8-hq due to steric effects and the small size of the Al^{3+} cation, but it rather forms heteroleptic complexes of the type $\text{ML}_2\text{L}'$. For example, [bis(2-methyl-8-quinolato)(4-phenylphenolato)Al(III)] (also known as BALq_2) emits blue

light, whereas the parent Alq_3 emits yellow-green light. Early interest in BALq_2 was based on it being a very good host for blue-light-emitting dopants (e.g., perylene), but it is now employed as a host as well as a hole blocker in red phosphorescent OLEDs [8].

We have been interested in OLEDs for nearly 20 years and in 8-hq derivatives as a means of manipulating the photoluminescence and the electronic properties of metal complexes. As such, we were interested in synthesising Li(I), Zn(II), Al(III), and Zr(IV) complexes of 2-tert-butyl-8-hydroxyquinoline (2-TB-8-hq). The synthesis of 2-TB-8-hq was first reported by Kazi in 1971 to afford a white crystalline solid (m.p. 72–73°C) in 20% yield [9]. In 1979, Kazi's report was disputed by Thompson and Stubley [10] who claimed to have isolated 2-TB-8-hq as a yellow liquid in 3.4% yield by direct reaction of tert-butyllithium with 8-hq and in 15% yield when a protective methylation-demethylation route was employed. In 2001, Delapierre et al. [11] concurred with Thompson and Stubley that 2-TB-8-hq was a yellow liquid, while achieving a higher yield of 42%.



SCHEME 1



SCHEME 2

This paper reports not only a simple, improved synthesis of 2-TB-8-hq as a crystalline solid (m.p. 73°C) in over 60% yield but also its crystal structure, resolving three decades of controversy and confirming that Kazi's report [9] was indeed correct.

2. Results and Discussion

Firstly, the preparation of 2-tert-butyl-8-hydroxyquinoline was attempted by protecting the 8-hydroxy group by methylation using methyl iodide and potassium carbonate, followed by treatment with tert-butyllithium at -78°C . The temperature was kept below -30°C for 1 h before allowing it to rise to room temperature. After the usual work-up of the reaction mixture which contains the dihydroquinoline, it was oxidised by refluxing with iodine in ethanol for 2 h. Finally, the demethylation was carried out using boron tribromide in dichloromethane at room temperature to give the required 2-TB-8-hq in 66% yield. See Scheme 1.

The procedure was later modified without the protection of the methyl group but by the addition of excess tert-butyllithium at -78°C as before. The lithium salt was carefully oxidized by bubbling air through the reaction mixture for 1 hour, during which the yellow suspension became an orange solution. Finally, the lithium derivative was hydrolysed by the addition of dilute hydrochloric acid to give the target compound 2-TB-8-hq in a comparatively moderate yield of 61%. See Scheme 2.

Since the latter method (Reaction Scheme 2) was found to be easier to carry out (experimental work-up) using less expensive chemicals, this alternative synthesis was utilised to scale the product up to 50 g and purified by column chromatography (ethyl acetate-petroleum ether (40– 60°C) [19:1]) in pure form (99%) as confirmed by gas chromatography and ^1H NMR spectroscopy. The colourless thick liquid obtained was triturated with petroleum ether (40– 60°C) and a few millilitres of ethyl acetate. Cooling the saturated solution in an ice bath gave a colourless crystalline solid form of 2-TB-8-hq (MP 73°C (DSC, onset)). Single crystal X-ray crystallography further confirmed its identity. The crystal structure of 2-TB-8-hq was found to be orthorhombic. The ORTEP diagram is shown in Figure 1.

We attribute the poor yield obtained by Kazi [9] to the fact that he did not fully oxidise the dihydroquinoline intermediate [A]: he did not bubble air or oxygen through the reaction mixture; neither did he add other oxidants. However, his observation that 2-TB-8-hq was solid with m.p. of 72°C is correct, and the authenticity of his compound was supported by elemental analysis results and NMR spectroscopy. We believe that the reason why Thompson and Stubley [10] and Delapierre et al. [11] obtained a yellowish liquid rather than a solid is due to the presence of impurities such as the intermediate [A] and the lithium complex [B] (see Reaction Scheme 2).

We synthesised the lithium complex of 2-TB-8-hq in accordance with our previously published method [12].

TABLE 1: Melting points, HOMO-LUMO values, band gaps, and photoluminescence of Li-8-hq, Li-2-Me-8-hq, and Li-2-TB-8-hq.

Compound	Melting point/ $^{\circ}\text{C}^{\text{a}}$	HOMO/ eV^{b}	LUMO/ eV^{b}	E_g/eV^{c}	Emission maximum/nm
Li-8-hq ^s	362	-5.00	-2.08	2.92 ± 0.04	491 ± 2
Li-2-Me-8-hq ^s	397	-5.60	-2.60	3.00 ± 0.03	485 ± 2
Li-2-TB-8-hq ^s	>400	-5.86	-2.82	3.04 ± 0.02	475 ± 2

^aFrom DSC. ^bObtained from cyclic voltammetry in 1 mM analyte, supporting electrolyte 0.1 M tetrabutylammonium tetrafluoroborate in dichloromethane. Pt working and Pt auxiliary electrodes and Ag/AgCl (reference electrode). ^cDetermined from the absorption edge of vacuum thermal evaporated thin films.

^sPurified by vacuum sublimation.

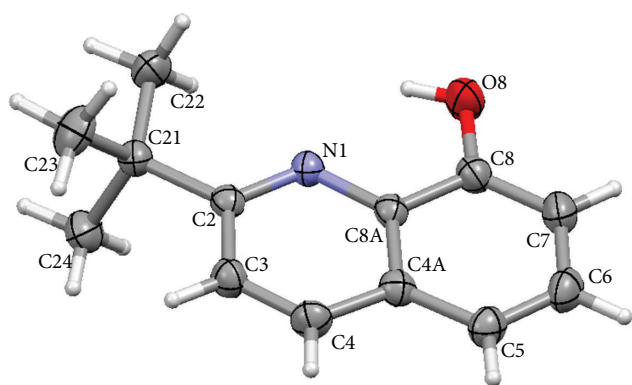


FIGURE 1: ORTEP diagram with atomic numbering scheme of 2-TB-8-hq. Ellipsoids are drawn at the 30% probability level.

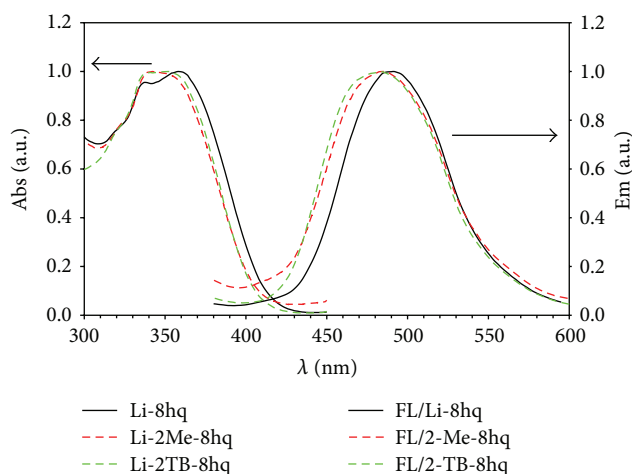


FIGURE 2: Absorption and fluorescence spectra of Li-8-hq, Li-2Me-8hq and Li-2TB-8hq.

These complexes are used in OLEDs as efficient electron injectors which evaporate at much lower temperature (280°C) than LiF which requires 550°C under vacuum thermal evaporation conditions. The vacuum thermal evaporated thin films of complex (Li 2-TB-8-hq), lithium 2-methyl-8-hydroxyquinolinolate (Li 2Me-8-hq), and lithium 8-hydroxyquinolinolate (Li 8-hq) have emission maxima at 475, 485, and 491 nm, respectively (Figure 2): full details will be published elsewhere. The blue shift in the emission wavelength upon 2-substitution is consistent with the presence of steric effects [5].

The electronic and thermal properties are summarised in Table 1.

The remarkable shift in the HOMO-LUMO values of 2-substituted 8-hq complexes shows that the electronic properties can easily be tuned by simple substitution at the 2-position of 8-hq. Similarly, preliminary experiments show that a methanolic solution of the bis complex $\text{Al}(\text{2-TB-8-hq})_2(o\text{-}^i\text{Pr})$ has an emission maximum at 442 nm in contrast to BALq_2 and Alq_3 which exhibit emission maxima at 490 and 509 nm, respectively. Further synthetic work is ongoing with the aim of preparing the BALq_2 analogue of 2-TB-8-hq.

3. Experimental Section

3.1. Synthesis of 2-Tert-butyl-8-hydroxyquinoline. 8-Hydroxyquinoline (25 g; 0.17 mole) in dry THF (100 mL) was cooled to -78°C . To the magnetically stirred solution, tert-butyllithium was slowly siphoned (1.7 M in hexane, 253 mL, 0.43 mole) under nitrogen atmosphere. The solution was kept below -30°C for 1 h and then allowed to rise to room temperature. The solution was then stirred and refluxed for 1 h and then cooled to room temperature. Air was bubbled through the mixture for 90 minutes, during which the light yellow solid in the solution disappeared and the solution became light red brown in colour. The reaction mixture was neutralised by the addition of dilute HCl (10%) and the product was extracted with dichloromethane ($3 \times 100\text{ mL}$). The combined organic phase was washed with brine and water and then dried over anhydrous magnesium sulphate. The solvent was evaporated under reduced pressure to give a light brown liquid.

The residue was purified by column chromatography over silica gel using ethyl acetate-petroleum ether ($40\text{--}60^{\circ}\text{C}$) [19 : 1] to give colourless liquid. Trituration with petroleum ether with a few drops of ethyl acetate gave a colourless crystalline solid (21 g, 61%). M.p 73°C (DSC, onset). Elemental analysis found: C, 77.86; H, 7.67; N, 7.13. $\text{C}_{13}\text{H}_{15}\text{NO}$ requires C, 77.58 H, 7.51, and N, 6.96%. ^1H NMR (500 MHz, CDCl_3) δ/ppm : 8.4 (1H, OH), 8.07 (1H, d, J 8.6 Hz, H-4), 7.54 (1H, d, J 8.6 Hz, H-3), 7.38 (1H, t, J 7.6 Hz, H-6), 7.28 (1H, dd, J 1.1 and J 8.2 Hz, H-5), 7.15 (1H, dd, J 1.2 and J 7.6 Hz, H-7), and 1.45 (9H, s, $-(\text{CH}_3)_3$). Mass spectrum: M^+ 201 (37%); 186, $\text{M}-\text{CH}_3$ (100); 159, $\text{M}-\text{C}(\text{CH}_3)_2$; 145, $\text{M}-\text{C}(\text{CH}_3)_3 + \text{H}$, and 117, $\text{M}-\text{CO}-\text{C}(\text{CH}_3)_3$ (10).

3.2. Preparation of 8-Methoxyquinoline. To a mixture of 8-hydroxyquinoline (10.0 g; 0.069 mole) and anhydrous potassium carbonate (48 g; 0.35 mole) in acetone (100 mL), methyl

iodide (5.2 mL; 0.083 mole) was added and stirred at room temperature for 18 h. The reaction was filtered and washed with acetone and the filtrate was evaporated. The residue was dissolved in dichloromethane (150 mL) and was washed with water. The organic phase was dried over anhydrous magnesium sulphate and solvent was removed to give a red-brown oil. The product was purified by column chromatography over silica gel dichloromethane-methanol [98 : 2] to give a low melting solid (10.2 g, 91%). Elemental analysis found: C, 74.87; H, 5.94; N, 8.59. $C_{10}H_9NO$ requires C, 75.45; H, 5.70 and N, 8.79%.

3.3. Preparation of 2-Tert-butyl-8-methoxyquinoline. 8-Methoxyquinoline (10 g; 0.063 mole) was dissolved in dry tetrahydrofuran (50 mL) and was cooled to -78°C . tert-Butyllithium (1.7 M; 45 mL; 0.076 mole) was added slowly and the reaction mixture was kept below -30°C for 1 h and was allowed to rise to room temperature. After stirring at room temperature for 18 h, the reaction mixture was poured into ice water and was extracted with dichloromethane (2×150 mL). The organic phase was washed with brine and water and was dried over anhydrous magnesium sulphate and solvent was removed to give a yellow orange liquid, 12 g. The TLC examination showed the absence of starting material.

The product was dissolved in ethanol (70 mL) and refluxed with iodine (18 g; 0.07 mole) for 2 h; solvent was removed and then was extracted with dichloromethane and 10% sodium thiosulphate. The organic phase after usual work-up was purified by column chromatography over silica gel ethyl acetate-petroleum ether ($40-60^{\circ}\text{C}$) [1 : 9] to give 2-tert-butyl-8-methoxyquinoline as a yellow oil (9.8 g, 77%). Elemental analysis found: C, 77.91; H, 8.12; N, 6.42. $C_{14}H_{17}NO$ requires C, 78.10; H, 7.96 and N, 6.50%.

3.4. Preparation of 2-Tert-butyl-8-hydroxyquinoline. 2-Tert-butyl-8-methoxyquinoline (9.8 g; 0.045 mole) was dissolved in dichloromethane (60 mL) and to the magnetically stirred solution at room temperature was added 1 M boron tribromide solution in dichloromethane (55 mL; 0.055 mole) under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 18 h, cooled in ice-water bath, carefully quenched with cold water, and finally extracted with dichloromethane. The organic phase was dried over anhydrous magnesium sulphate and solvent was removed to give a greenish liquid. This was purified by column chromatography over silica gel ethyl acetate-petroleum ether ($40-60^{\circ}\text{C}$) [1 : 9] to give a light yellow liquid which on cooling gave a colourless solid (6.0 g, 66%). M.p 73°C , DSC (onset). Elemental analysis found: C, 77.39; H, 7.51; N, 6.83. $C_{13}H_{15}NO$ requires C, 77.58; H, 7.51 and N, 6.96%.

Crystal Data for 2-TB-8-hq. $C_{13}H_{15}NO$, $M = 201.26$, orthorhombic, $a = 12.5619(6)$, $b = 11.1072(7)$, $c = 16.0684(7)$ Å, $U = 2242.0(2)$ Å³, $T = 295(2)$ K, space group $Pbca$, $Z = 8$, 4106 reflections measured, 2175 unique ($R_{\text{int}} = 0.041$). Final R_1 [$F > 4\sigma(F)$] = 0.0597, $wR_2(F^2) = 0.157$ (all data).

4. Conclusions

In conclusion, we have proven that 2-TB-8hq is indeed a solid (m.p. 73°C) and can easily be synthesised in high yield. It is not a liquid as some authors have previously reported [10, 11], solving the three decades of controversy. We have also made the same ligand by an alternative methylation route and obtained crystalline solid with 66% yield. The lithium complex of 2-TB-8-hq is blue-emitting and the HOMO and LUMO levels are lowered by 0.86 eV and 0.74 eV, respectively, compared with the parent Li 8-hq.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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